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# Hydrochemical system analysis of public supply well fields, to reveal water-quality patterns and define groundwater bodies: The Netherlands

Igor Mendizabal · Pieter J. Stuyfzand ·  
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**Abstract** Hydrochemical system analysis (HCSA) is used to better understand the individual state of and spatial patterns in groundwater quality, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones within each hydrosome (facies). The origin is determined by environmental tracers or geomorphological and potentiometric maps, the facies by combining age, redox and alkalinity indices. The HCSA method is applied to all 206 active public supply well fields (PSWFs) in The Netherlands, resulting in the distinction of nine hydrosomes and eleven facies parameters—age (young, intermediate, old), redox ((sub)oxic, anoxic, deep anoxic, mixed) and alkalinity (very low, low, intermediate and high). The resulting classification of PSWFs provides a means to (1) predict their vulnerability; (2) optimize groundwater-quality monitoring programs; and (3) better delineate groundwater bodies, by considering groundwater origin and flow. The HCSA translates complex hydrochemical patterns into easily interpretable maps by showing PSWFs, groundwater bodies and hydrochemical facies. Such maps facilitate communication between researchers, water resources managers and policy makers and can help

to solve complex groundwater resources management problems at different scales, ranging from a single well (field) or region to the national or European scale.

**Keywords** Groundwater monitoring · Groundwater protection · Tracing · Water management strategies · The Netherlands

## Introduction

A public supply well field (PSWF) is defined as a coherent set of pumping wells delivering groundwater to be distributed to the public as drinking water, either without or after treatment. The chemical and microbiological composition of the raw (untreated) mixed groundwater from a PSWF is to be initially assessed or periodically monitored in compliance with the relevant national drinking-water act—Safe Drinking Water Act 1974 (US EPA 1974); Water Framework Directive 2000 (EU 2000). Thereby, PSWFs constitute an attractive (inter)national monitoring system for evaluating the chemical state of groundwater. Advantages may consist of long data records, extensive analytical programs, and representativity for the relatively large volumes of water pumped, which are registered as well. Mendizabal and Stuyfzand (2009) also mention the disadvantages: (1) the chances on bias in using data from a well field, (2) historical changes in both the well field and the hydrochemical methods applied, and (3) the mixing of groundwater of different composition, origin and age.

The hydrochemical data resulting from PSWF monitoring are included in the regular reporting of European Union (EU) member states to the EU Commission, in compliance with the Groundwater Directive (2006), daughter of the Water Framework Directives 2000 and 2008 (EU 2000; 2008). The reason is that these data also supply very useful information on the groundwater environment, which in the opinion of the EU Commission should not degrade any further.

Thus, hydrochemical data from PSWFs are collected on a large scale and have been so for a long time. They have been extensively used in national groundwater

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surveys on for instance nitrate (Brooks and Cech 1979; Goss et al. 1998; Kross et al. 1993; Rudolph et al. 1998; Stuart et al. 1995), fluoride (Lalumandier and Jones 1999; Stas et al. 1937), bromide (Davis et al. 2004), iodine (Gezondheidsraad 1932), arsenic (Stuyfzand et al. 2008), lanthanides (de Boer et al. 1996), carcinogens (Cech et al. 1988) and pesticides (Reed 1987; Squillace et al. 2002). What is lacking, however, is a systematic approach that combines all relevant data into a clear typology of the raw groundwater pumped by a PSWF, so as to better understand the individual state of and spatial patterns in groundwater quality. This enables optimization of water-quality monitoring programs, well-head protection measures and well-field adaptation procedures.

The aim of this contribution is to present such a systematic approach to combine all relevant data into a clear typology of PSWFs and to illustrate its capabilities by applying it to all 206 PSWFs active in The Netherlands in 2008. The method departs from the hydrochemical facies analysis (HyFA) introduced by Stuyfzand (1990, 1999) and renamed *hydrochemical system analysis* (HCSA) by Stuyfzand (2006) as a means to map and diagnose all major factors accounting for regional variations in hydrochemistry, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The HCSA should not be confused with the well known groundwater flow-systems analysis introduced by Toth (1963) and Engelen and Jones (1986). A groundwater flow system may transport various hydrosomes and a hydrosome may even exist, as palaeogroundwater, without flow (Stuyfzand 1999).

The methodology presented here is a modified version of the original HCSA, in order to better address the mapping of PSWFs, by defining the hydrochemical facies as a combination of indices for the age, redox and alkalinity of the pumped water. The origin of the water is to be determined by environmental tracers and geomorphological and potentiometric maps. Here, the HCSA is also used to create a chemical typology of PSWFs. Although presented for The Netherlands, the HCSA can be applied to any network of PSWFs worldwide.

## Setting and methods

### Hydrogeological setting of The Netherlands

The major fresh groundwater resources in The Netherlands are contained in unconsolidated sediments of Tertiary and Quaternary age, composed of alternating layers of marine, eolian, fluvial, paludal and glacial origin. A unique, moderately large fresh groundwater body in consolidated rock is observed in Cretaceous limestone in the south-east of the country (Fig. 1). These major groundwater bodies are recharged in the Holocene coastal dunes, the northern, eastern, central and southern Pleistocene uplands, and the Cretaceous limestone hills (inset of Fig. 1).

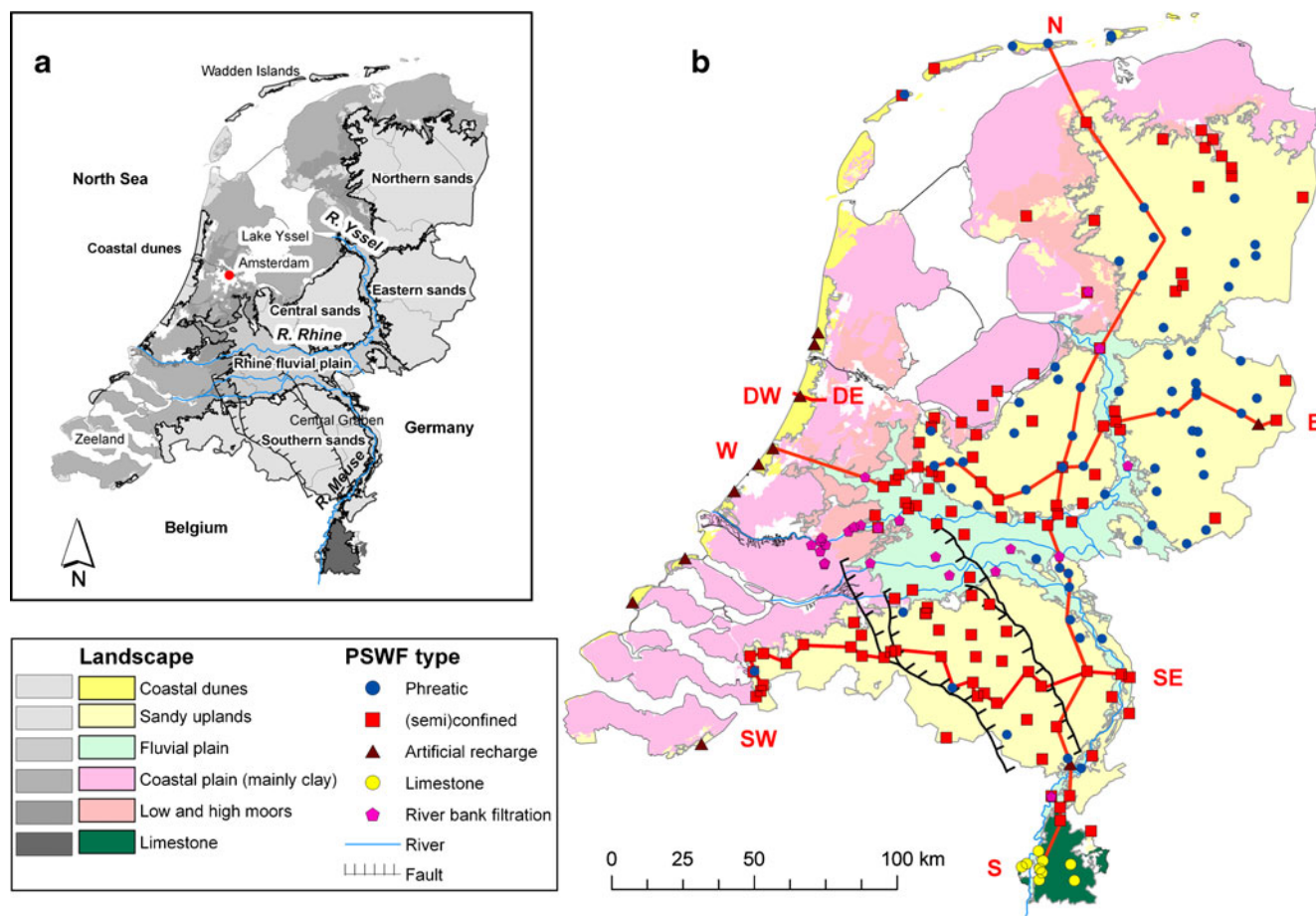
The hydrogeological structure of The Netherlands and the depth to the fresh-brackish interface (here defined as 1,000 mg Cl/L) are shown in three hydrogeological cross sections (Fig. 2). The freshwater resources in the coastal dune belt along the North Sea coast extend down to a maximum depth of 50–130 m BSL (below sea level). Those in the Pleistocene uplands reach depths of 100–250 m BSL in the Northern sands, 10–100 m BSL in the Eastern sands, 150–280 m BSL in the Central sands, and 100–500 m BSL in the Southern sands (Fig. 2). The one in the Cretaceous hills has its base at 20–100 m BSL. The shallow position of the interface in the eastern uplands coincides with a shallow position of impermeable Tertiary clays. The deepest position of the interface in the southern uplands is tectonically determined by the Central Graben (Figs. 1 and 2), a deep tectonic graben structure in which coarse sands prevail down to a depth of 400–600 m BSL.

Groundwater resources have been supplemented by artificial recharge (AR) systems mainly in the coastal dunes and by river bank filtration (RBF) along the rivers Rhine and Meuse. Drinking water is also prepared by direct intake of surface water from these rivers and from Lake Yssel (19% of a total annual production of 1,187 Mm<sup>3</sup> in 2004); those plants are not addressed in this study.

### PSWFs and their data collection

The active 206 PSWFs in The Netherlands have initially been classified as indicated in Table 1, on the basis of the origin of the groundwater and the properties of the aquifer (Fig. 1). Some further characteristics are mentioned in Table 1 as well. These data derive from the National Network of Public Supply Well Fields, an extensive database containing numerous properties of all Dutch PSWFs and the raw water quality and volumes pumped since 1898 (Mendizabal and Stuyfzand 2009). Most PSWFs consist of vertical PVC wells, with an average borehole diameter of around 60 cm (+/– 15 cm gravel pack) and an average screen length of 15–30 m. The use of PVC, which is advantageous because of insensitivity to corrosion, is quite unique worldwide as it was enhanced by the presence of a PVC manufacturer in The Netherlands (C. van Beek, KWR Watercycle Research Institute, personal communication, 2010). The wells within a PSWF are distributed following different geometrical patterns. PSWFs can either tap one or various aquifers, but every independent well is usually screened in a single aquifer. The water is mainly lifted by underwater pumps (positive displacement), but also by suction (both individually and in groups). Well technical details can be found in Makkink et al. (2000).

During a national sampling campaign in the first trimester of 2008, all active PSWFs were sampled for chemical analysis. Samples were collected following the guidelines described in Mendizabal and Stuyfzand (2009), in order to obtain the hydrochemically most representative samples for the well field. Samples were taken from faucets on the transport mains that discharge the water from various or all pumped wells, when these wells had been active for at least a couple of hours. In well fields



**Fig. 1** Location map of **a** The Netherlands and **b** the 206 PSWFs active in 2008, their hydrological type (according to Table 1) and the main recharge areas of groundwater pumped for public drinking-water supply. The positions of the profiles depicted in Figs. 2, 4 and 5 are indicated

where the storage capacity of the pumping station limited the number of wells that could simultaneously abstract water, the most representative selection of wells was switched on for obtaining a representative sample of the well field. In PSWFs tapping both phreatic and confined aquifers, two samples were collected, representative for each aquifer. Thus, a total of 241 samples was obtained from the 206 active PSWFs, including the ones obtained from a part of a PSWF.

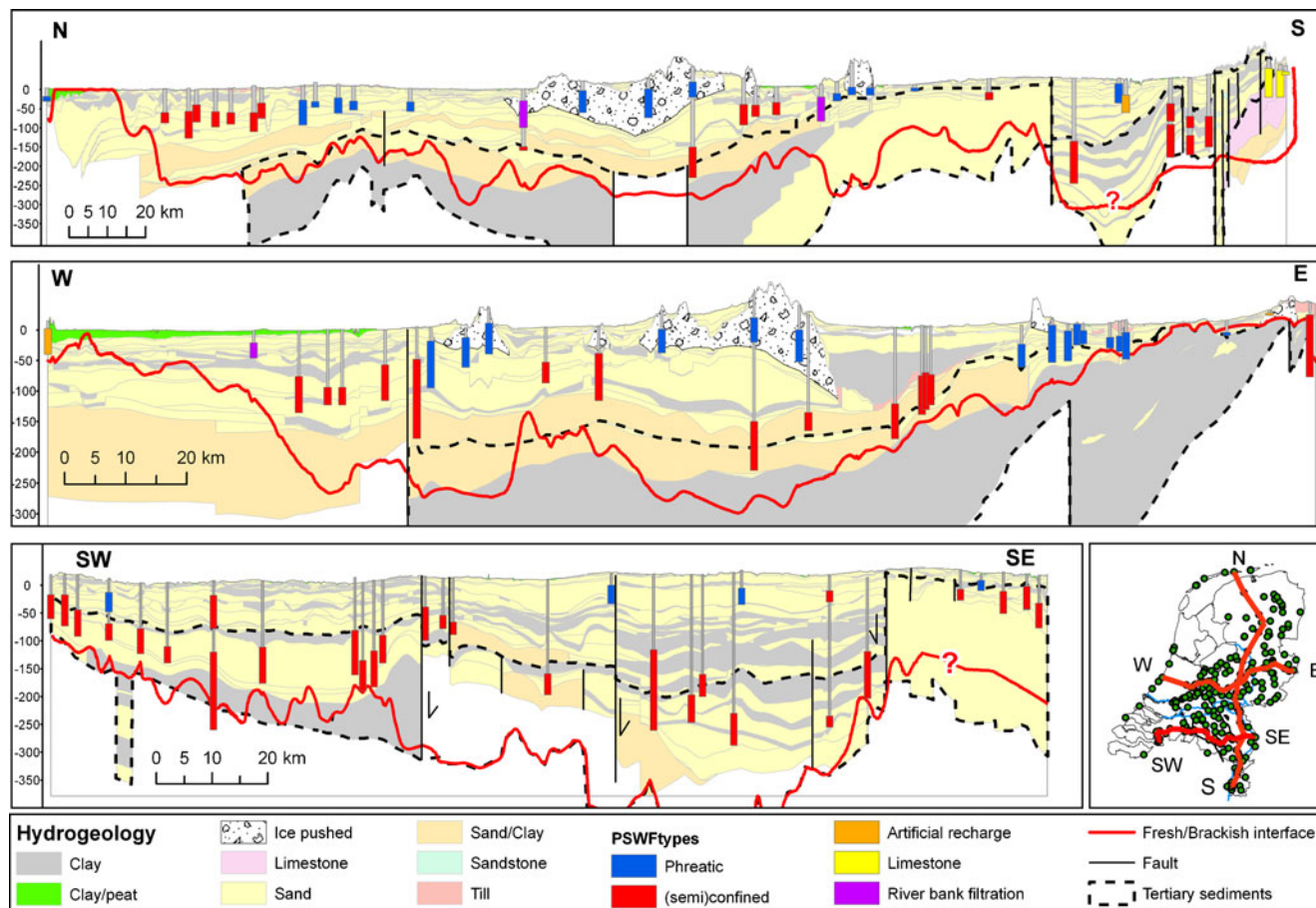
Samples were analyzed for a wide package of parameters, including amongst others, macroparameters (cations, anions and nutrients), trace elements and the stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ . Temperature, specific electrical conductivity (SEC), pH and dissolved oxygen were measured on site. Eh (electrode potential for redox state) was omitted because, unfortunately, it cannot be measured unambiguously in most natural waters (Appelo and Postma 2005). On site determination of Eh runs into practical problems and is handicapped by unreliable results (Lindberg and Runnells 1984) or difficulties in quantitative thermodynamic interpretation (Peiffer et al. 1992). Therefore, the suggestion by Stumm (1984) was followed to deduce the redox level from all redox sensitive main components of water. Samples for analysis of cations,  $\text{PO}_4$ ,  $\text{SiO}_2$  and trace elements were collected in

100-ml polypropylene bottles, after filtration in the field through a 0.45- $\mu\text{m}$  millipore membrane filter, and acidified to  $\text{pH} < 2$  by addition of 0.7-ml  $\text{HNO}_3$  Suprapur 65%. They were analyzed by inductively coupled plasma-mass and optical emission spectrometry (ICP-MS + ICP-OES). Samples for analysis of  $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{HCO}_3$ ,  $\text{NO}_3$ ,  $\text{NO}_2$  and  $\text{NH}_4$  were collected unfiltered in 100-ml polypropylene bottles and stored in a refrigerator for less than 3 days before analysis by spectrophotometry. Sulphide ( $\text{HS}^-$ ) was not measured because of expected low concentration levels, expected problems with sample preservation and financial limitations. Samples for analysis of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  were collected in 30-ml brown glass bottles without filtration and without any preservative. The bottles were fully filled and hermetically closed to avoid atmospheric gas exchange. The samples were kept in the dark and at  $4^\circ\text{C}$  until analysis by mass spectrometry.

### Hydrochemical system analysis

The hydrochemical system analysis (HCSA) developed by Stuyfzand (1990, 1999, 2006) yields a water typology and maps with the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome.





**Fig. 2** Hydrogeological cross sections over The Netherlands with the location and depth of abstraction (in m BSL) of PSWFs, in the directions N–S, W–E and SW–SE. PSWFs simplified to a single screen covering the entire depth of abstraction of individual pumping wells. The *color* of the well screen indicates the type of PSWF as defined in Table 1. The inset location map shows the position of the cross sections and active PSWFs in 2008. Hydrogeological data obtained from REGIS II.1 (Vernes and van Doorn 2005). The fresh–brackish water interface (1,000 mg/L Cl) is given by the *red line* (estimated by expert judgment around the *question marks*, due to lack of data). The *dashed line* encloses sediments of Tertiary age

### Hydrosomes

A hydrosome (also called hydrochemical groundwater system or groundwater body) is defined as a coherent, three-dimensional unit of groundwater with a specific

origin. Its borders can be determined by geomorphological, land elevation and potentiometric maps and/or environmental tracers and geo-electrical soundings, provided enough observation wells are available.

**Table 1** Hydrological classification of PSWF-types in The Netherlands, with data referring to the year 2008. The number of PSWFs corresponds to the number of samples obtained during sampling (phreatic and confined parts of a PSWF pumping both aquifers are sampled separately and further considered as two PSWFs)

PSWF type	Sand and gravel		AR	RBF	Limestone
	G Phreatic	(Semi)confined			
Number of PSWFs	67	126	12	27	9
Mean raw-water production per PSWF (Mm <sup>3</sup> /year) <sup>a</sup>	2.8	3.7	16.0	2.7	2.6
Total amount of drinking water produced (Mm <sup>3</sup> /year) <sup>a</sup>	187	449	192	74	23
% of total amount of drinking water produced <sup>a</sup>	20	49	21	8	3
Mean number of wells/collection points	11	12	131	17	7
Mean land surface (LS)(m ASL)	18	14	9	3	68
Mean abstraction level (m BLS)	26–60	82–135	11–31	24–56	24–74
Mean aquifer level (m BLS)	10–89	69–156	5–44	20–68	14–99
Mean aquifer thickness (m)	80	88	40	48	85
Mean depth to brackish water (m)	154	204	65	142	197
Age spectrum (y)	2–200	20–25,000	0.1–0.3	1–50	2–200

<sup>a</sup> Water production in year 2004; *G* fresh, autochthonous, actual groundwater; *AR* artificially recharged water; *RBF* river bank filtrate; *LS* land surface; *ASL* above sea level; *BLS* below land surface

A 'hydrosome complex' is composed of various adjacent hydrosomes with a very similar origin and recharge area. The complex members cannot be easily discerned from each other with environmental tracers. A 'hydrosome type' is characterized by a similar type of recharge water, like river water in case of RBF or AR hydrosomes. Hydrosomes belonging to the same type may have a totally different chemistry because of different source waters (for instance the Rhine River, Meuse River or Lake Yssel) and they do not need to be adjacent.

PSWFs may tap from different hydrosomes, mainly in the following cases: (1) AR and RBF well fields that inevitably also pump autochthonous groundwater; (2) salinizing well fields where minor quantities of, for instance intruding, recent seawater or upconing, saline palaeogroundwater mix with fresh groundwater; and (3) well fields abstracting from different aquifers in zones where different freshwater hydrosomes are interfingering. In these cases, for the sake of producing simple robust maps while using available hydrochemical and geo-electrical data, the boundaries for PSWF hydrosomes are defined as follows: (1) AR if >20% infiltrated, pretreated surface water; (2) RBF if >20% infiltrated river or lake water; and (3) autochthonous fresh groundwater if  $\text{Cl} < 1,000 \text{ mg/L}$ . The boundary of  $1,000 \text{ mg Cl/L}$  is constrained to the availability of data.

In the following, an explanation of how to identify Rhine River bank filtrate and quantify its contribution to well fields in the Rhine fluvial plain by inorganic multi-tracing is given. The same environmental tracers are valid to identify pretreated Rhine water in AR systems. Meuse river water, either in AR or RBF systems, is more difficult to recognize and may require the simultaneous use of both inorganic tracers (other than those for Rhine water) and organic tracers (persistent micropollutants).

#### *Identification and quantification of Rhine river bank filtrate*

Stuyfzand (1989) and Mendizabal and Stuyfzand (2009) identified Rhine RBF amidst autochthonous groundwater in the Rhine fluvial plain of The Netherlands by means of  $\delta^{18}\text{O}$ , Cl, the Cl/Br ratio and Mg. Of all the tracers,  $\delta^{18}\text{O}$  is the best single tracer of Rhine RBF. Its use relies on the contrasting low  $\delta^{18}\text{O}$  of Rhine water (on average  $\delta^{18}\text{O} = -9.85\text{‰}$ ; Mook 1968), as compared to autochthonous groundwater in The Netherlands with an average  $\delta^{18}\text{O}$  of  $-7.6\text{‰}$  (Stuyfzand 1989). The difference is related to the high contribution (ca. 70%) of the inland mountainous areas in Switzerland and Germany to the Rhine's discharge in The Netherlands, and the depletion of the heavier oxygen isotope  $\delta^{18}\text{O}$  upon its preferential raining out from oceanic air when moving inland and uphill.  $\delta^{18}\text{O}$  levels in autochthonous groundwater, however, may deviate from  $-7.6\text{‰}$ , especially when infiltrated during a glacial period ( $-9\text{‰}$ ) or when infiltrated in swampy areas with high evaporation losses ( $-4$  to  $-6\text{‰}$ ), and due to differences in distance to the North Sea coastline (0.5–250 km), altitude ( $-7$  to 321 m ASL) and/or land use. On the other hand,  $\delta^{18}\text{O}$  levels in the Rhine may also deviate

from  $-9.85\text{‰}$  due to spatial and temporal variations. Higher values (up to  $-9.45\text{‰}$ ) relate to smaller river branches with more evaporation and receiving exfiltrating groundwater. A recent trend of increasing  $\delta^{18}\text{O}$  levels in the Rhine ( $-9.85\text{‰}$  in the 1960–1970s, to  $-9.1\text{‰}$  in the period 1997–2006) is noted as a result of climate change and various changes in water management in the Rhine catchment area (Stuyfzand 2008b).

The second best tracer of Rhine RBF is the Cl/Br ratio. Rhine water has a significantly higher Cl/Br ratio (600–700, on a mg/L basis) than normal fresh and salt groundwater in The Netherlands (300). The anomaly is caused by the low Br content of salt waste from the salt mining industry in the Elzas region, which is discharged into the Moesel River, a tributary of the Rhine River. The ratio is less reliable than  $\delta^{18}\text{O}$ , due to more complications. On the one hand, raised levels in autochthonous groundwater are encountered in urbanized areas, because of leaky sewer systems and/or road de-icing salt (Kelly 2008). On the other hand, levels in RBF can be lower, mainly by the release of Br from organic rich muds that accumulate where river flow is reduced (Stuyfzand et al. 2006), and by abstraction of old RBF with a Cl/Br ratio  $\leq 300$  because it infiltrated before the salt mining industry started.

Other valid tracers for Rhine RBF, in addition to Cl and Mg, are molybdenum (Mo) and SEC, because their levels are significantly raised in the Rhine River due to various pollution inputs. Mo is present as the relatively mobile anion molybdate, which is sensitive to sorption and reductive precipitation. Thus, raised Mo concentrations are strong indicators of Rhine RBF, whereas low levels are less diagnostic because they may indicate either autochthonous groundwater or little-flushed, deep anoxic RBF systems. SEC, which is not conservative either, is a strong indicator of autochthonous groundwater from the central uplands, provided its value is very low (due to infiltration in the strongly leached sandy uplands) and the RBF is relatively young and polluted.

All these tracers can be individually used to quantify the percentage of RBF in the pumped water and the complications inherent to each of them can be reduced by combining them in a multitracing approach. The multitracing approach consists of the separate use of selected tracers, with due consideration of their boundary conditions, and averaging their results with a weighting factor  $W$  that depends on the tracer contrast (Table 2).

The percentage of RBF according to tracer X (%RBF<sub>X</sub>) pumped by a PSWF is quantified by

$$\% \text{RBF}_X = 100 \frac{(C_M - C_G)}{C_R - C_G} \quad (1)$$

where:  $C_M$  = tracer concentration in sample,  $C_G$  = average concentration in autochthonous groundwater;  $C_R$  = tracer concentration in the river bank filtrate.

$C_G$  and  $C_R$  are to be calculated as the average concentration of PSWFs (or preferably monitoring wells) that are a priori known (by potentiometric mapping, hydrological modeling and previous multitracing) to pump

**Table 2** Tracer concentrations used in Eq. 1 for quantifying the percentage of river bank filtrate pumped by PSWFs in the Rhine fluvial plain.  $W$  weight assigned to each tracer;  $C_P$  tracer concentration in precipitation.  $C_G$  tracer concentration in autochthonous groundwater;  $C_F$  tracer concentration in Rhine River water;  $C_R$  tracer concentration in RBF.  $S_x$  standard deviation of X. The number of PSWFs used to calculate average values of  $C_G$  and  $C_R$  are given in brackets

Tracer application				Groundwater (100%)			Rhine water (>90%)		
Tracer	Units	Condition <sup>a</sup>	$W$	$C_P$	$C_G$ (13)	$S_G$	$C_F$	$C_R$ (12)	$S_R$
Cl	mg/L	B	1.00	5	13	4	120	105	7
Mo	μg/L	C	0.50	<0.1	0.2	0.1	1.5	1.3	0.2
$\Delta^{18}O$	‰	A	0.47	-7.6	-7.1	0.5	-9.85	-9.6	0.2
Mg	mg/L	B	0.33	0.3	5	2	11	11	1
Cl/Br ratio	mg/L	B	0.29	293	292	48	650	485	35
EC	μS/cm 20°C	B	0.29	31	273	123	700	749	84
B	μg/L	B	0.23	<5	21	22	80	80	11

<sup>a</sup> Condition:

A waters should be younger than 5,000–10,000 years (condition fulfilled in all cases); B as A, + Rhine water should have infiltrated after ca. 1953 without contacting thick underwater muds, and + groundwater should be without significant urban, industrial or agricultural impacts; C as B, + calculated %RBF<sub>Mo</sub> is always a minimum value

100% groundwater and >90% RBF respectively. Concentrations in RBF are preferred among concentrations in river water, in order to take into account eventual changes of non-conservative parameters during infiltration. Concentrations obtained for both end-member groups are listed in Table 2, together with their standard deviation (respectively  $S_G$  and  $S_R$ ) and mean values of their recharge water.

The average %RBF resulting from multitracing (%RBF) then becomes:

$$\%RBF = \frac{\sum W_x \%RBF_x}{\sum W_x} \quad (2)$$

where the weighting factor  $W_x$  for tracer X is defined as follows:

$$W_x = \frac{\left\{ \frac{|C_R - C_G|}{\sqrt{S_R S_G}} \right\}_{\text{TRACER X}}}{\text{Max} \left\{ \frac{|C_R - C_G|}{\sqrt{S_R S_G}} \right\}_{\text{ALL TRACERS}}} \quad (3)$$

where  $S_R$  and  $S_G$  are the standard deviation of tracer X in, respectively, river bank filtrate and groundwater.

Equation 3 is an intuitive equation, the results of which have been tested against the results of a student *t*-test. This test yielded a very similar ranking of tracers. However, the values obtained with Eq. 3 can be used directly, while those of the *t*-test can not. The absolute value of the difference in concentrations divided by the geometric mean of the standard deviations is a measure of the contrast of a tracer in both end members. The denominator is used to normalize the weights to values between 0 and 1. The weighting factor obtained is also a good indication of the performance of every independent tracer. Equations 1 and 3 can be extended to account for situations where the raw water delivered by the PSWF is composed of a mixture of not just two waters (the usual case) but of three or more.

As already mentioned, every tracer has its own complications and its successful application is constrained to the conditions listed in Table 2. In all cases, waters should be younger than 5,000–10,000 years. All tracers except for  $\delta^{18}O$  are constrained to the condition that (1) Rhine water should have infiltrated after ca. 1953, without

contacting thick underwater muds; and (2) groundwater should be free of any significant urban, industrial or agricultural impact. Additionally, the % RBF calculated as based on Mo is always a minimum value, due to sorption and reductive precipitation.

#### Hydrochemical facies

Within a given hydrosome, the chemical composition of water varies in time and space, due to changes in recharge composition and in flow patterns, and due to chemical processes between water and its porous medium. Such variations in chemical character can be used to subdivide a hydrosome into characteristic zones or ‘hydrochemical facies’, a term introduced by Back (1960). The concept of geochemical facies and the use of geochemistry in determining groundwater origins, ages and flow systems is widely discussed by Glynn and Plummer (2005). In mapping a coastal aquifer system, Stuyfzand (1999) defined the facies on the basis of calcite saturation classes, and a redox, pollution and base exchange index. In mapping AR and RBF systems, Stuyfzand (2006) chose pH classes and the redox and pollution index. In the case of PSWFs, it is proposed to define the facies by combining age, redox and alkalinity indices.

**Age index.** The age index designates the possibility of relatively recent anthropogenic pollutants. It is derived from the percentage of ‘young’ groundwater (%Y) that infiltrated after 1953 (thus <55 years old in 2008): O (old) if %Y < 5%, I (intermediate) if %Y = 5–50%, and Y (young) if %Y > 50%. The year 1953 is chosen because it divides the ‘old’ period with negligible  $^3H$  activities (at present) and relatively low pollution levels, from the ‘young’ period with relatively high  $^3H$  activities and pollution levels. The %Y is obtained from the hydrological response curve of the well field as calculated by a calibrated groundwater model when available, or otherwise as approximated analytically by Mendizabal and Stuyfzand (2009). Their method combines a calculation based on the depth to the water table, top and base of the well screen, average groundwater recharge rate and



porosity, with a single tritium measurement of the raw water and the tritium record of the recharge water.

**Redox index.** The redox index determines the oxidation or reduction state of the groundwater and thereby the mobility of heavy metals and organic micropollutants (Chapelle 2001; Stuyfzand 1998; 2006). Due to the practical problems of onsite measuring methods of Eh (Appelo and Postma 2005) and difficulties in quantitative thermodynamic interpretation (Peiffer et al. 1992), the redox level was deduced, as suggested by Stumm (1984), from all redox sensitive main components of water, i.e.  $O_2$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $H_2S$ , Fe, Mn,  $NH_4^+$  and  $CH_4$  (Stuyfzand 1993, 2006). Similar redox classifications were presented by Chapelle (2001), but these do not define the ‘mixed’ redox class, which is rather common in water samples obtained from PSWFs (10% of the samples obtained for this study), due to the local mixing of waters from different origins and redox environments, which occurs within the pumped well. The indicated redox clusters (sub)oxic (o), anoxic (a), deep anoxic (d) and mixed (m) are chosen here, because of limitations of data availability (especially regarding  $O_2$ ,  $H_2S$  and  $CH_4$ ) and the need to avoid maps that are too complex. The redox clusters (sub)oxic, anoxic and deep anoxic follow a logical succession within a hydrosome in the direction of groundwater flow. The redox cluster ‘mixed’ is assigned when samples contain antagonistic redox sensitive main components of water (like  $NO_3^-$  and  $Fe^{2+}$ ) above a specific threshold concentration (Table 3).

**Alkalinity index.** The alkalinity index is an excellent geochemical reaction progress variable, especially regarding the dissolution of carbonates and the oxidation of organic matter. It derives from alkalinity classes in a chemical water-type classification (Stuyfzand 1989). They are defined on a 2-log scale in meq ( $HCO_3^- + CO_3^{2-}$ )/L: 0–0.5, 0.5–1, 1–2, 2–4 etc. Here, four alkalinity classes are defined: 0–1, 1–2, 2–4 and >4 meq (Table 4).

**Facies coding.** Each facies is denoted by a code consisting of the succession of the three indices. In order to reduce the number of facies codes on the map, those indices are not displayed which are considered ‘standard state’ of the hydrochemical system. The standard state is: intermediate age, anoxic, and high alkalinity. For instance, young, anoxic, low alkalinity groundwater is coded as Y2.

## Results

In The Netherlands, the spatial distribution of hydrosomes has been investigated by Engelen (1981), Stuyfzand (1989, 1993), Griffioen and van der Aa (2002) and Beusen et al. (2008). From their work, the seven hydrosome complexes and two hydrosome types listed in Table 5 are considered relevant for PSWFs. All PSWFs are abstracting groundwater from these nine hydrosomes. The predominant hydrosome is indicated for each PSWF in Fig. 3, together with the score for the three facies indices as derived from their water analysis.

Based on these data, three-dimensional maps of groundwater bodies and hydrochemical facies were produced on a national scale. Figure 4 shows the extension of hydrosomes with depth and the hydrochemical facies within every hydrosome in three cross sections over the country. The fresh–brackish interface (for practical reasons defined at 1,000 mg Cl/L) was used as the lower boundary of hydrosome mapping. Brackish and salt hydrosomes are, thus, not further differentiated here, nor are those fresh hydrosomes that lack any abstraction by a PSWF.

Transboundary hydrosomes occur along the eastern and southern border of The Netherlands, with recharge areas in Germany and Belgium respectively. Those from Germany are incorporated into the adjacent Dutch hydrosome complex because of similar quality. Those from Flanders (northern Belgium) constitute a separate hydro-

**Table 3** Practical criteria for the determination of the redox index—slightly modified after Stuyfzand (1993). Concentrations in mg/L

Level	Environment	Criteria (mg/L)						
		$O_2$	$NO_3^-$	$Mn^{2+}$	$Fe^{2+}$	$SO_4^{2-}$	$H_2S^a$	$CH_4$
0	Oxic	$O_2 \geq 0.9 (O_2)_{sat}$		<0.1	<0.1	$\geq 0.9 (SO_4)_o$	No	<0.1
1	Penoxic ( $O_2$ -reducing)	$1 \leq O_2 < 0.9 (O_2)_{sat}$		<0.1	<0.1	$\geq 0.9 (SO_4)_o$	No	<0.1
2	Suboxic ( $NO_3^-$ -red)	<1	$\geq 1$	<0.1	<0.1	$\geq 0.9 (SO_4)_o$	No	<0.1
3	Transition (Mn-red)	<0.5	<1	$\geq 0.1$	<0.1	$\geq 0.9 (SO_4)_o$	No	<0.1
4	Iron reducing	<0.5	<0.5		$\geq 0.1$	$\geq 0.9 (SO_4)_o$	No	<0.1
5	Sulphate reducing	<0.5	<0.5			A	Yes	<1
6	Methanogenic	<0.5	<0.5			B		$\geq 1$
Redox clusters:								
o	(Sub)oxic	0–2	$O_2$	$NO_3^-$	$Mn^{2+}$	$Fe^{2+}$	$SO_4^{2-}$	$H_2S^a$
a	Anoxic	3–4	$\geq 1$ or	$\geq 1$	<0.1	<0.1		No
d	Deep anoxic	5–6	<0.5	<0.5		$\geq 0.1$	$\geq 0.9 (SO_4)_o$	No
m	Mixed <sup>b</sup>	M	$\geq 1$ or	$\geq 1$	$\geq 0.15$ or $\geq 0.15$	C	Yes or	$\geq 0.5$ or

<sup>a</sup> Yes/no = yes/no clear  $H_2S$ -smell in field

<sup>b</sup> Sample composed of a mix of water from different redox environments

$[O_2]_{sat} = 14.594 - 0.4 t + 0.0085 t^2 - 97 \times 10^{-6} t^3 - 10^{-5} (16.35 + 0.008 t^2 - 5.32/t) Cl$ , with  $t$  = temperature in °C and Cl in mg/L

$A = 0.1[SO_4]_o < SO_4 < 0.9[SO_4]_o$ , if  $Cl \leq 300$  mg/L and else  $0.5[SO_4]_o \leq SO_4 < 0.9[SO_4]_o$ ;

$B = SO_4 \leq 0.1[SO_4]_o$  or  $SO_4 \leq 3$ , if  $Cl \leq 300$  mg/L or  $SO_4 < 0.5[SO_4]_o$  if  $Cl > 300$  mg/L;

$C = SO_4 \leq 0.9[SO_4]_o$  or  $SO_4 \leq 3$ , if  $Cl \leq 300$  mg/L;  $[SO_4]_o$  = original  $SO_4$  concentration in mg/L



**Table 4** Hydrochemical facies descriptors with their code and value

Index	Facies code	Facies descriptor	value	Standard state
Age	Y	Young	>50%Y	No
	I <sup>a</sup>	Intermediate <sup>a</sup>	5–50%Y <sup>a</sup>	Yes <sup>a</sup>
	O	Old	<5%Y	No
Redox	o	(sub)oxic	0–2	No
	a <sup>a</sup>	Anoxic <sup>a</sup>	3–4 <sup>a</sup>	Yes <sup>a</sup>
	d	Deep anoxic	5–6	No
	m	Mixed	0–6	No
Alkalinity	1	Very low	0–1 meq/L	No
	2	Low	1–2 meq/L	No
	3	Moderate	2–4 meq/L	No
	4 <sup>a</sup>	High <sup>a</sup>	>4 meq/L <sup>a</sup>	Yes <sup>a</sup>

<sup>a</sup>Standard state facies (if standard state, then the facies code is omitted from the map for simplicity)

some due to clear quality deviations resulting from lithological differences of the outcropping Tertiary sediments. Table 6 summarizes exploitation data for each hydrosome in 2008, regarding exclusively PSWFs.

Well-field managers should consider the individual quality of PSWFs in terms of the contributing hydrosome(s) and the hydrochemical facies within its catchment area (see section Discussion). In order to understand structural differences between well-field types or hydrosomes, and for a compact reporting to water authorities, it does make sense to also show, in Table 7, the average water quality of the nine hydrosomes as pumped by PSWFs. In order to better differentiate between hydrosomes, some of them have been subdivided: hydrosomes I and U on the basis of a different origin of the infiltrating surface water—respectively Rhine (r), Meuse (m), Yssel (y) and other (o); and hydrosomes C, N and S on the basis of a different alkalinity and redox facies in deep PSWFs (alkalinity index 3 or 4 and redox index “a” or “d”) and shallow PSWFs were differentiated otherwise. The nine hydrosomes are briefly described in the following, in alphabetical order.

BSL) contain extremely low contents of reactive phases like calcite, pyrite or organic matter. This, in combination with a land use dominated by nature reserves, results in a high quality of the pumped water, which most frequently shows a young, (sub)oxic, low alkalinity facies (Fig. 4; N–S and W–E). The composition is unique in The Netherlands with its low TDS, total hardness, alkalinity and concentrations of K, B, Ba, F and Li. Total hardness and alkalinity are often below drinking water standards of respectively 1 mmol/L and 60 mg/L (Water Supply Act 2001; Dutch Ministry of Environment 2001). The lack of stronger acidification phenomena in most PSWFs is due to the slow advance of young, more acid water thanks to a relatively thick unsaturated zone (5–38 m) and low recharge rates due to the predominance of pine woods. Therefore, only a few PSWFs present raised concentrations of Al and lanthanides by dissolution of Al-silicate minerals at lowered pH (Table 7). In the deeper, more reactive parts of the aquifer system, composed of calcareous marine sediments of Tertiary to early Pleistocene age, the dominant facies changes into old, deep anoxic water with high alkalinity.

### The Central hydrosome complex (C)

The largest and highest ice-pushed sandy hill area in The Netherlands constitutes the main recharge area of this hydrosome. The upper layers (roughly down to 50–70 m

### The Coastal Dune hydrosome complex (D)

This hydrosome complex extends all along the North Sea coast of The Netherlands, including the Islands of Zeeland,

**Table 5** Hydrosome complexes (HC) and types (HT) in The Netherlands and their main characteristics

Code	Hydrosome	Origin <sup>a</sup>	Source <sup>b</sup>	Aquifer material <sup>c</sup>	Sediment age <sup>d</sup>	Depositional environment <sup>e</sup>	% confined
C	Central sands (HC)	P	G	S	P	G/F	25
D	Coastal dunes (HC)	P	G	S	H	E/M	70
E	Eastern sands (HC)	P	G	S	P	G/F	0
F	Flanders (HC)	P	G*	S	T	M/F	100
I	Artificial recharge (HT)	R	AR	S	H	E/M	0
L	Limestone (HC)	P	G	L	C	L	20
N	Northern sands (HC)	P	G	S	P	G/F	90
S	Southern sands (HC)	P	G	S	P	F	30
U	River bank filtration (HT)	R	RBF	S	P	F	60

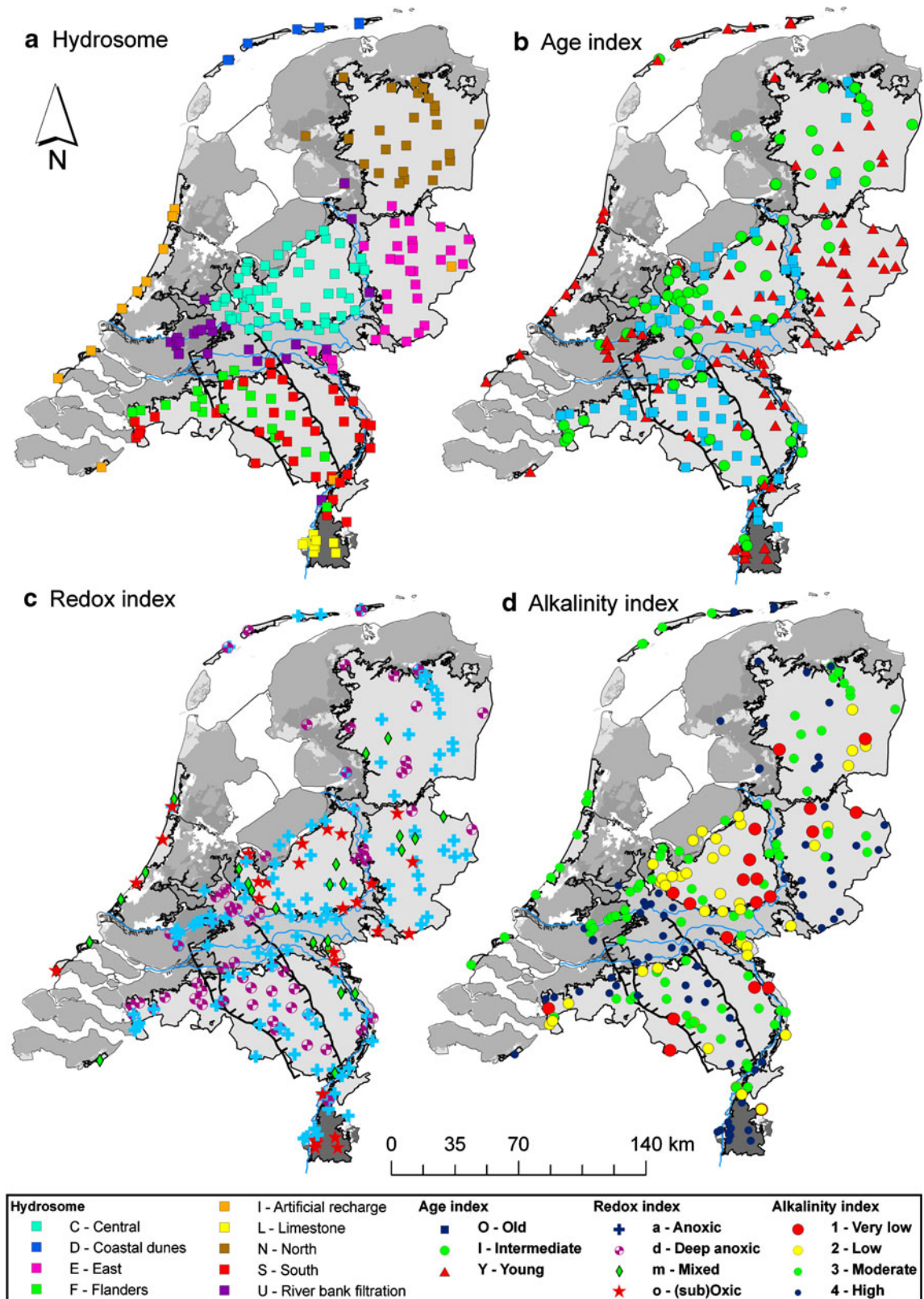
<sup>a</sup>Origin: P precipitation; R river (or lake)

<sup>b</sup>Source: G autochthonous groundwater <1,000 years old, with local recharge; G\* autochthonous groundwater >1,000 years old; AR artificially recharged water; RBF river bank filtrate

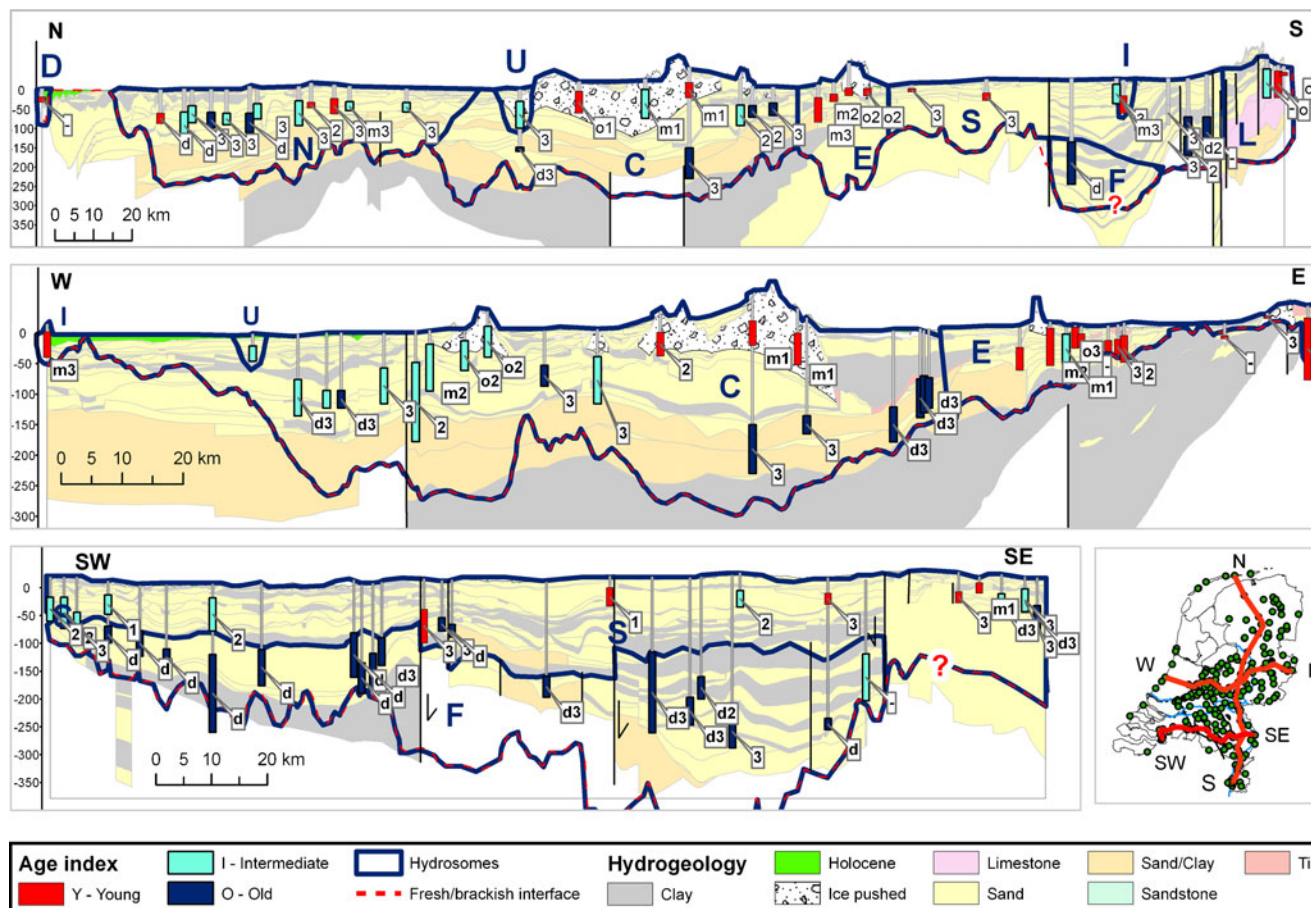
<sup>c</sup>Aquifer material: S sand and gravel; L limestone;

<sup>d</sup>Sediment age: P Pleistocene (+Tertiary); H Holocene (+Pleistocene); T Tertiary; C Late Cretaceous

<sup>e</sup>Depositional environment: E eolian; F fluvial; G glacial; L lagunal; M marine



**Fig. 3** Spatial distribution of **a** hydrosomes assigned to all PSWFs active in The Netherlands in 2008 and the three hydrochemical facies indices: **b** age, **c** redox, **d** alkalinity



**Fig. 4** Hydrogeological cross sections *N-S*, *W-E* and *SW-SE* over The Netherlands with the spatial distribution of hydrosomes (groundwater bodies) and well-screen position of public supply well fields (PSWFs). The *color* of the well screen indicates the age index. The *labels* show the hydrochemical facies assigned to each PSWF (legend in Table 5). The *inset* location map shows the location of the cross sections and all active PSWFs in 2008. Hydrogeological data obtained from REGIS II.1 (Vernes and van Doorn 2005)

the coastal mainland and the Wadden Islands. The freshwater lenses, up to 130 m BSL, are surrounded by intruded North Sea water and relict Holocene transgression waters (Stuyfzand 1993). Numerous PSWFs pumped dune water during the late nineteenth and the twentieth centuries, but most of them have been closed down, or have been transformed in the 1950s into AR systems, due to severe salinization. Today, the only PSWFs abstracting 100% dune water are situated in the Wadden Islands. They mainly consist of nature reserves and yield groundwater of high quality, characterized by calcite equilibrium (high pH, Ca and  $\text{HCO}_3$ ), high sea-spray inputs (Cl, Br, Na, K, Mg and  $\text{SO}_4$ ) and cation exchange due to a historical expansion of the freshwater lens (high K and Mg). They present the highest  $\text{SiO}_2$  concentrations of all PSWFs, due to the leaching of biogenic opal (marine diatoms) from Holocene marine, fine-grained deposits below the dunes. All PSWFs are anoxic to deep anoxic and belong to alkalinity groups 3–4.

### The Eastern hydrosome complex (E)

A shallow, calcareous and pyritiferous sandy aquifer on top of impervious Tertiary clay layers accommodates this thin hydrosome complex. PSWFs mainly pump young ground-

water which on several sites is strongly affected by agricultural activities (high  $\text{NO}_3$ ,  $\text{SO}_4$ , Cl and K). There, the high  $\text{NO}_3$  loads and declining water tables triggered the oxidation of pyrite, which is reflected in the raised concentrations of  $\text{SO}_4$ , Fe, As, Co, Ni and Zn. The relatively high inputs of acidity via pyrite oxidation and atmospheric deposition are largely buffered by calcite dissolution. Consequently, pH, total hardness and  $\text{HCO}_3$  are relatively high, necessitating the addition of an expensive water-softening step to the purification system. In the central parts, groundwater is horizontally mixed with shallow oligomineral water (water with low TDS) from small ice-pushed ridges, poor in reactive phases such as calcite, pyrite or organic matter. This evening out of different qualities makes the averaged data in Table 7 less informative than the facies maps in Figs. 3 and 4. The main facies within the Eastern hydrosome is, however, Ya4 (Fig. 3).

### The Flanders hydrosome complex (F)

In the south of The Netherlands, PSWFs abstract water from two different systems (Fig. 4; *N-S* and *SW-SE*): deep, confined groundwater of Tertiary age, either infiltrated in Flanders (Belgium) or in the Dutch province of Brabant, and



**Table 6** Average exploitation data for the nine hydrosomes in The Netherlands in 2008, regarding exclusively PSWFs

Hydrosome	C	D	E	F	L	N	S	I	U
Number of PSWFs	52	7	31	29	9	27	42	12	32
Mean raw-water production per PSWF (Mm <sup>3</sup> /year) <sup>a</sup>	3.3	0.1	2.8	5.1	2.6	5.1	2.5	15.5	2.6
Total amount of drinking-water produced (Mm <sup>3</sup> /year) <sup>a</sup>	168	1	86	142	23	126	105	186	82
% of total amount of drinking water produced <sup>a</sup>	18	0.1	9	15	3	14	11	20	9
Mean number of wells/collection points	9	10	13	12	7	18	10	131	16
Mean land surface (LS) (m ASL)	15	4	22	11	68	8	24	9	3
Mean abstraction level (m BLS)	63–116	21–33	23–53	130–195	24–74	53–94	58–107	11–31	31–62
Mean aquifer Level (m BLS)	42–154	10–36	7–72	122–222	14–99	33–134	50–117	5–44	28–74
Mean aquifer thickness (m)	112	27	65	99	85	101	67	40	46
Mean depth to brackish water (m)	221	59	98	230	197	164	208	65	149
% of PSWFs yielding specific age:									
Young water	17	86	94	0	100	22	21	100	50
Intermediate age water	38	14	6	0	0	56	38	0	38
Old water	44	0	0	100	0	22	36	0	13
% of PSWFs yielding specific redox:									
(Sub)oxic	21	0	19	0	56	0	0	33	9
Anoxic	40	57	55	3	44	56	83	8	75
Deep anoxic	25	43	6	97	0	37	10	0	13
Mixed	13	0	19	0	0	7	2	58	3
% of PSWFs yielding specific alkalinity:									
Very low alkalinity	15	0	13	0	0	7	14	0	0
Low alkalinity	37	0	19	3	0	15	29	0	0
Moderate alkalinity	38	57	19	28	0	41	33	92	59
High alkalinity	10	43	48	69	100	37	19	8	41

<sup>a</sup> Water production in year 2004

younger groundwater systems of local recharge belonging to the Southern hydrosome complex (discussed in the following).

PSWFs recharged in Flanders have been identified by their deep anoxic character ( $\text{SO}_4 < 1 \text{ mg/L}$ ), their age (0% water younger than 55 years), their low Cl concentration (about 6 mg/L when excluding PSWFs with salinization due to upconing) and their low Cl/Br ratio. PSWFs of this group abstract deep anoxic water from 50 to 250 m depth, with an estimated age in the order of 1,000–10,000 years. The normal modern  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  levels indicate that the water must have infiltrated after the last glacial period, whereas low  $^{14}\text{C}$  activities—10–30 percent modern carbon (pmc); data not shown—point to an age  $> 1,000$  years. Some of them might pump groundwater recharged in Germany or Limburg (in the southern part of The Netherlands). The presence of glauconite and apatite in several aquifer layers is suspected to be responsible for relatively high As, B and Li concentrations. Some PSWFs show salinization phenomena (raised concentrations of Cl, Br and Na), due to upconing of connate salt water from fine-grained marine deposits of early Pleistocene and late Tertiary age (Stuyfzand and Stuurman 2008). The Cl/Br ratio is relatively low, especially in the samples without salinization, probably due to the more inland position of the recharge area which is known to reduce this ratio (Davis et al. 2004). All PSWFs in the Flanders hydrosome are old, deep anoxic waters of high alkalinity (Facies Od4).

### Artificially recharged hydrosomes (I)

Most “I” hydrosomes are situated in the coastal dunes, in nature reserves. The chemical composition of every I

hydrosome strongly reflects the quality of the pretreated surface water used for its artificial recharge. This means that there are large differences between the hydrosomes recharged by water from the Rhine River, Lake Yssel, Meuse River and a small brook in the south-west. On average, they yield groundwater in equilibrium with calcite, with high concentrations of Cl, Br,  $\text{SO}_4$ , Na, K, Ca, Mg, F, Mo and specific organic micropollutants (data not shown), and low concentrations of  $\text{SiO}_2$ . The infiltrated Rhine River water can be easily recognized in the coastal dunes by combination of its low  $\delta^{18}\text{O}$  content and high Cl/Br ratio (Stuyfzand 2008b). The tracer contrast between these water types is quite different from the one between Rhine river bank filtrate and autochthonous groundwater in the Rhine fluvial plain (Table 2).

Most I hydrosomes belong to alkalinity group 3 and present a (sub)oxic or mixed redox index. The mixed redox is due to the mixing of anoxic with (sub)oxic infiltrate and the admixing of both deep anoxic and (sub) oxic autochthonous groundwater in the recovery system, which occurs within the pumped well.

### The Limestone hydrosome complex (L)

This hydrosome complex corresponds to a 100-m-thick layer of karstified Cretaceous limestone covered by Pleistocene loess and fluvial gravels and underlain by Carboniferous shale (Fig. 4; N–S and SW–SE). The groundwater has the highest concentrations of Ca and  $\text{HCO}_3$ , and the highest SEC, TDS and total hardness of all (Table 7). This obviously relates to the dissolution of calcite in an environment with high  $\text{CO}_2$  pressures (in



**Table 7** Median water quality of PSWFs belonging to the nine hydrosomes defined

Hydrosome <sup>a</sup>		Recharged by local rain water									Recharged by river water							
		C <sub>d</sub>	C <sub>s</sub>	D	E	F	L	N <sub>d</sub>	N <sub>s</sub>	S <sub>d</sub>	S <sub>s</sub>	I <sub>m</sub>	I <sub>r</sub>	I <sub>y</sub>	I <sub>o</sub>	U <sub>m</sub>	U <sub>r</sub>	U <sub>o</sub>
Number of PSWFs		23	29	7	31	25	9	20	7	27	19	4	4	3	1	2	28	2
EC	uS/cm	324	196	556	526	392	774	471	294	455	252	482	613	700	616	525	701	730
pH	-	7.8	7.4	8.0	7.1	7.4	7.1	6.9	6.5	7.1	6.5	7.7	7.6	7.8	7.3	6.5	7.3	7.1
Temp	°C	12.0	10.0	9.5	10.5	12.3	11.5	10.7	10.2	11.8	11.2	12.7	10.4		10.7	11.7	12.0	11.5
Cl	mg/L	12	15	77	28	9	26	27	24	18	11	42	81	105	33	34	100	64
HCO <sub>3</sub>	mg/L	161	85	242	222	255	367	248	92	241	99	170	179	167	273	193	229	358
NO <sub>3</sub>	mg/L	0.0	4	0	0	0	16	0	0.1	0	0	5	6	3.0	2.2	14	0	0.0
SO <sub>4</sub>	mg/L	1	17	7	63	0.3	54	1	25	11	24	53	53	61	79	71	45	15
Ca	mg/L	50	34	76	90	65	136	78	37	78	38	70	79	73	114	89	83	109
Mg	mg/L	5	3	12	8	6	14	7	4	9	4	8	11	11	7	8	11	12
Na	mg/L	13	10	42	18	11	9	18	14	18	8	32	46	68	20	23	54	34
K	mg/L	1.3	1.0	3.5	2.4	3.7	2.3	1.8	1.7	3.8	1.8	5.9	5.0	5.5	12.4	3.9	4.9	3.7
Fe	mg/L	0.72	0.04	0.30	0.51	2.14	0.08	6.98	8.54	5.29	7.40	0.18	0.09	0.22	0.50	0.02	2.57	9.40
Mn	mg/L	0.09	0.04	0.10	0.19	0.07	0.00	0.25	0.35	0.18	0.10	0.07	0.03	0.07	0.32	0.00	0.52	0.47
NH <sub>4</sub>	mg/L	0.3	0.01	0.5	0.2	0.6	0.0	0.4	0.1	0.5	0.1	0.11	0.1	0.1	0.32	0	1	3.2
PO <sub>4</sub>	mg/L	0.5	0.2	1	0.3	0.8	0.2	1.0	0.8	0.9	0.4	0.3	0	0.2	0.1	0.1	0.9	1.8
SiO <sub>2</sub>	mg/L	18	14	33	15	21	27	26	19	20	18	7	7	8	11	11	16	20
Al	ug/L	1	1	3	1	1	1	1	1	1	2	0.5	1	0.5	2	0.5	2	4
As	ug/L	0.3	1.2	0.3	0.9	1.3	0.3	0.3	1.3	0.9	0.3	3.4	2.8	1.5	1	0.3	1.3	1.5
B	ug/L	17	6	49	15	39	13	15	10	53	7	52	51	70	52	43	77	38
Ba	ug/L	18	10	2	42	12	40	58	42	51	39	50	23	91	82	81	92	99
Br	ug/L	44	44	222	62	32	50	71	51	52	36	118	192	179	144	87	201	160
Co	ug/L	0.02	0.0	0.02	0.03	0.01	0.02	0.0	0.9	0.0	0.0	0.35	0.20	0.2	0.52	0.07	0.08	0.11
Cu	ug/L	0.7	2.1	0.2	0.9	0.2	0.9	0.2	0.3	0.3	0.3	2.0	1.5	1.2	18.6	1.5	1.1	0.7
F <sup>b</sup>	ug/L	50	70	140	70	110	170	70	80	100	65	295	120	120	210		117	136
Li	ug/L	3.0	1.7	7.4	3.8	8.3	11.5	5.5	3.9	13.4	5.4	6.2	10.0	11.7	4.1	5.0	8.5	4.6
Mo	ug/L	0.2	0.2	0.2	0.2	0.1	0.8	0.1	0.1	0.1	0.1	2.0	1.7	1.6	1.0	0.1	0.8	0.2
Ni	ug/L	0	0	0.1	0.7	0.1	0.7	0	1.8	0.2	0.9	2.1	1.3	0.7	3.9	0.6	0.8	0
Sr	ug/L	165	92	352	261	247	379	210	107	344	114	272	445	427	419	191	456	359
Zn	ug/L	3	7	0.9	5	2	2	3	5	5	8	6	15	45	14	5	2	2
δ <sup>18</sup> O	‰	-7.2	-7.5	-6.7	-7.1	-6.9	-7.7	-6.0	-6.8	-6.9	-7.2	-6.2	-9.2 <sup>c</sup>	-6.8	-6.4	-6.8	-9.4	-6.0
δ <sup>2</sup> H	‰	-49	-48	-47	-47	-46	-52	-41	-46	-46	-47	-42	-64	-49	-45	-45	-66	-43
ΣLan	mg/L	0.08	0.08	0.09	0.1	0.08	0.07	0.1	0.07	0.09	0.18	0.12	0.12	0.11	0.21	0.11	0.11	0.22
Cl/Br	mg/L	292	345	308	438	278	466	323	410	329	298	358	425	559	229	387	464	394
SI <sub>calcite</sub>	-	0.1	-0.7	0.4	-0.1	0.1	0.1	-0.5	-1.6	-0.3	-1.5	0.1	0.1	0.2	0.1	-0.9	0	0.0
BEX	meq/L	0.58	0.26	1.05	0.61	0.81	0.89	0.44	0.37	0.92	0.43	0.92	0.595	0.81	0.77	0.75	0.6	0.61
TDS	mg/L	307	171	439	460	378	653	412	222	432	180	391	460	493	542	435	518	612
TH	mmol/L	1.4	1.0	2.4	2.6	2.0	3.9	2.2	1.1	2.3	1.1	2.1	2.4	2.3	3.1	2.5	2.5	3.2
TIC	mmol/L	2.9	1.5	4.0	4.7	4.6	7.4	5.7	2	4.6	2	2.9	3.1	2.8	5.0	5.5	4.2	7.2

<sup>a</sup> Hydrosomes subdivided in: *d* deep; *s* shallow; *r* Rhine; *m* Meuse; *y* Yssel; *o* other river<sup>b</sup> Measured in 1992<sup>c</sup> Average value for infiltrated Rhine water deriving from tributary Lek

ΣLan sum of all lanthanides; SI<sub>calcite</sub> saturation index for calcite; BEX base exchange index calculated as the meq-sum of the typically marine cations Na, K and Mg, corrected for a contribution of sea salt according to BEX=Na+K+Mg-1.0716 Cl—after Stuyfzand (1993); TDS total dissolved solids; TH total hardness (Ca+Mg+Sr); TIC total inorganic carbon (CO<sub>2</sub>+HCO<sub>3</sub>+CO<sub>3</sub>)

loess) and a high atmospheric deposition of acidifying SO<sub>2</sub> due to proximity of major industrial emission centers in Germany (Ruhr Gebiet), Belgium (Liege) and The Netherlands (DSM). Also highest are the NO<sub>3</sub> concentrations, which derive from agricultural emissions that meet insufficient reduction capacity in the fast circulating upper parts of the limestone aquifer. The concentrations of SO<sub>4</sub>, Mg, F, Li, Mo and Sr as well as the Cl/Br ratio are remarkably high as compared to the other hydrosomes without AR and RBF. This may relate to high atmospheric inputs (SO<sub>4</sub> and F), high geochemical inputs (Mg, F and Sr from limestone), and contributions from urbanized areas or infiltrating surface waters (Li, Mo and Cl/Br ratio). The limestone hydrosome presents the facies Y and Yo (Fig. 3).

### The Northern hydrosome complex (N)

The Northern hydrosome complex is recharged on a sandy plateau largely composed of glacial till with few isolated terminal moraines and small ice-pushed hills, and with wide-spread occurrences of thin eolian cover sands. Originally much high-moor peat formed in areas where the glacial till aquitard hindered dewatering, but little peat remained after excavation for six centuries. The deeper groundwaters (older than 100 years) still present some characteristics of groundwater infiltrated through peat soils and with effects of open-water evaporation, showing high Fe, NH<sub>4</sub> and PO<sub>4</sub> concentrations and high δ<sup>2</sup>H and δ<sup>18</sup>O levels (column N<sub>d</sub> in Table 7). The low CaCO<sub>3</sub> contents of the upper sediments are responsible for the relatively low concentrations of Ca,

Sr and  $\text{HCO}_3$  and low pH and  $\text{SI}_{\text{calcite}}$  in the shallow phreatic PSWFs (column N<sub>s</sub> in Table 7). Most PSWFs deliver anoxic to deep anoxic water of intermediate to old age.

### The Southern hydrosome complex (S)

The Southern hydrosome complex comprises PSWFs pumping from Pleistocene and Tertiary sandy aquifers overlain by eolian fine sands (Fig. 4). The spatial variability in reactive minerals of the locally deposited sediments yields a large heterogeneity within this hydrosome, which displays most of the discerned hydrochemical facies. The Southern hydrosome is divided in two groups in Table 7. Group S<sub>d</sub> corresponds to PSWFs pumping deep confined Tertiary aquifers in the Central Graben (Fig. 1 and Fig. 4; N–S and W–E) that deliver old, unpolluted water of good quality, similar to the Flanders hydrosome. They also present high As, B and Li concentrations possibly released from glauconite, but they differ in higher Ba, Br, Cl, Sr,  $\text{SO}_4$  and Zn concentrations. Group S<sub>s</sub> corresponds to shallower PSWFs, some of them characterized by a low alkalinity (groups 1 and 2 in Fig. 3). The ones with alkalinity <0.5 meq/L show high concentrations of Al, due to the dissolution of aluminum hydroxides. In these acidic environments trace elements are also mobilized, notably Be, Cd, Co, Cu, Lu, Y and Zn, together with all lanthanides. Most PSWFs to the east also present signs of pyrite oxidation, analogous to the Eastern hydrosome.

### River bank filtrate hydrosomes (U)

This hydrosome type is composed of bank filtrate from the Rhine River (28 PSWFs), the Meuse River (2 PSWFs) and two lakes. The major occurrences are located in the western part of the Rhine fluvial plain (most PSWFs in the eastern part pump autochthonous groundwater because the Rhine drains the area there). Water quality is, like in the case of artificial recharge, mainly dictated by the influent river (or lake), which shows an increased pollution record until the 1970s, when sanitation measures in the drainage basins started to have significant effects (RIWA 2002).

The hydrosomes composed of Rhine River bank filtrate present the highest B and Ba concentrations of all hydrosomes, and they contain more Cl, Br, Na, Mo and Sr but less  $\delta^{18}\text{O}$  than the river bank filtrates from the Meuse and lakes. This is explained by a higher pollution load with B, Ba and Mo, the discharge of Br depleted salt waste into the Moesel River by salt mines in the Elzas area, and a large contribution of snow melt from the Alps.

The different types of RBF nicely range from (sub)oxic (Meuse) to (deep) anoxic (Rhine) to deep anoxic (lakes) in the global direction of surface water flow (Stuyfzand et al. 2006): a steep river gradient and coarse gravels along the Meuse are more conducive to maintaining (sub)oxic aquifer conditions, than where flow is more reduced and the sediments are finer-grained. All PSWFs of the river bank filtrate hydrosome present moderate-to-high alkalinity.

Most of them are anoxic, but all the redox classes are represented.

## Discussion

### Vulnerability of PSWFs

The HCSA offers direct insight into the vulnerability of PSWFs towards specific fluvial pollution hazards (if the hydrosome type is either ‘artificial recharge’ or ‘river bank filtration’), and towards those environmental pollution hazards that strongly depend on the three indices used to define the hydrochemical facies. How these indices relate to vulnerability is explained in the following.

The age index is a good indicator of vulnerability towards all hazardous compounds released at the surface. PSWFs delivering ‘young’ water are potentially vulnerable, while PSWFs delivering ‘old’ waters are much less vulnerable because of the longer travel time, which delays the pollution front and increases the chance of sorption and (bio)degradation or decay. Old PSWFs are, however, often more vulnerable towards marine salinization from deeper layers, due to a shorter distance between the well screen and the fresh–brackish interface.

The alkalinity index gives an indication of the vulnerability towards acidifying processes. In calcareous aquifers (alkalinity index 3 or 4), the acid is very effectively buffered by calcite dissolution raising the concentrations of Ca and  $\text{HCO}_3$  and, thus, hardening the raw water. Hardening is mainly a problem in the Limestone hydrosome and in the Eastern and Southern hydrosomes, where total hardness reaches values above 3 mmol/L. In non-calcareous aquifers (alkalinity index 1 or 2), the acidity is buffered by the soil and aquifer in a less desirable way, not by calcite dissolution, but by a successive base exchange, the dissolution of silicate minerals, Al- and Fe-hydroxides. This results, when pH drops below 5–6 and alkalinity below about 1, in substantial concentration increases for Al and positively charged trace elements like Be, Cd, Co, Cu, Ni, Pb, Y, Zn and lanthanides.

The redox index is a measure of the capacity of the aquifer to reduce undesired oxidants like  $\text{NO}_3$ ,  $\text{SO}_4$ , (per)chlorate and  $\text{Cl}_2$ , and to eliminate specific pollutants through by-products of reduction (like  $\text{H}_2\text{S}$  which triggers the precipitation of many metal sulfides), reductive dehalogenation (chlorinated hydrocarbons) or specific oxidation or reduction processes (many organic micropollutants including pesticides and pharmaceuticals).

(Sub)oxic PSWFs are more vulnerable than (deep) anoxic PSWFs, for example, to elevated  $\text{NO}_3$  and  $\text{SO}_4$  concentrations and those agrichemicals that resist biodegradation in a (sub)oxic environment. Anoxic or deep anoxic PSWFs are, on the other hand, more vulnerable than (sub)oxic PSWFs to As mobilizing from iron(hydr)oxides that reductively dissolve, and to those hydrophilic organic micropollutants in river water that resist biodegradation in a (deep) anoxic river bank but not in a (sub)oxic environment. A mixed redox PSWF is highly vulnerable to chemical well clogging, which is usually

caused by precipitation of Fe and Mn hydroxides after mixing aerobic and anaerobic waters.

### Optimizing the monitoring program

The PSWF typology resulting from the HCSA also constitutes a valuable tool for optimizing groundwater-quality monitoring programs. The typology yields information on the origin of the water, the hydrogeochemical environment and the potential proximity of anthropogenic (modern) pollutants. This information helps to fine-tune the monitoring program to those parameters that are likely to be found in a specific water source and in a specific environment. Some guidelines to optimize the monitoring network are listed in Table 8.

PSWFs pumping young water should have a more frequent monitoring program with a wider analytical package than PSWFs pumping old water. PSWFs with a mixed redox index should analyze for a broader range of redox sensitive compounds because they receive inputs from both (sub)oxic and (deep) anoxic environments. Analogously, PSWFs with a specific redox index are likely to yield concentrations under the minimum detection limit (MDL) of the analytical method for a range of parameters, which could be monitored with a lower frequency. Following these guidelines based on the HCSA, costs are minimized and benefits maximized.

### Reflections on 'groundwater bodies' as defined for EU

According to the Water Framework Directive (EU 2000; EU 2008), EU state members must define and characterize bodies of water, based on stream basins (SB) for surface water and groundwater bodies (GWB) for groundwater. In order to facilitate the relation between surface and groundwater for ecological restoration purposes, the definition of GWBs is constrained to the previously defined SBs so that each GWB must fully lie within the boundaries of a SB. Following these guidelines, seven SBs and 23 GWBs were defined in The Netherlands (SGBP 2009).

The resulting GWBs might be adequate from a European perspective, but present some inconsistencies on a national scale, because: (1) constraining the definition of GWBs to the boundaries of SBs may divide waters of the

same origin and hydrogeological system into different GWBs; (2) a groundwater flow system can contain various hydrosomes such as artificially recharged surface water and autochthonous groundwater; and (3) according to the horizontal guidance document on water bodies (EU 2003), the delineation of GWBs should be based on geological boundaries to flow, so that any groundwater flow from one body to another is so minor that it can be ignored or can be estimated with adequate precision.

The HCSA overcomes these problems and yields more homogeneous GWBs, which are more logically delimited for water-quality protection purposes and for answering international questions on transboundary aquifers. These GWBs are also better extrapolated in depth following the groundwater flow system, rather than a simple vertical extrapolation of the SB limits. Such vertical extrapolation introduces large errors, for example, in sandy aquifers overlain by clay and/or peat layers, where groundwater is mainly recharged through horizontal flow from neighboring sandy aquifers. In such areas (which are common in The Netherlands and elsewhere in Europe), the geographically established boundaries of the SBs are not consistent. The boundaries could be improved there by means of a HCSA, either applied to PSWFs as presented here, to observation wells, or both. Another urgent reason to apply the HCSA is the differentiation between groundwater *sensu stricto* and GWBs with AR and RBF, which are rapidly increasing in number and volume in many countries by the popularity of these methods for the production of clean safe drinking water. In the authors' opinion, such managed aquifer recharge systems and their effect on groundwater quality should be more thoroughly characterized within the Water Framework Directive, analogous to the effect of groundwater exfiltrating into surface water, which is considered a crucial cause of eutrophication of surface-water ecosystems.

Regarding PSWFs, groundwater bodies used for the production of drinking water must be registered in the 'Register protected areas'. Such bodies are defined as (1) bodies of water used for the abstraction of water for human consumption which provide more than an average of 10 m<sup>3</sup>/day in total, or which serve more than 50 persons, and (2) bodies of water intended for such level of use in the future (Water Framework Directive 2000; EU 2000). Member states must guarantee the production of drinking water from the pumped water with the current

**Table 8** Hydrogeochemical screening program for groundwater analysis, in sequential order—modified after Stuyfzand (Stuyfzand 1998)

Origin (detection by Cl <sup>-</sup> , Cl/Br, $\delta^{18}\text{O}$ , EJ)	Analyze specific OM <sub>s</sub> and trace elements only in specific waters (Na-dikegulac in Rhine bank filtrate; Ag, Hg, Mo, Pb, Se, Sn, U in leachate of mine tailings)
Alkalinity index	If alkalinity index 3 or 4, do not analyze for Al, Be, lanthanides, Sc, Ti
Redox index (by O <sub>2</sub> , NO <sub>3</sub> , SO <sub>4</sub> , CH <sub>4</sub> , EJ)	If deep anoxic, do not analyze for: Ag, Cd, Co, Cu, Hg, Ni, Pb, Se, Zn, AOX/VOX, chloro-alkanes and chloro-alkenes
Age index (determined by either hydrological calculations or tracing methods ( <sup>3</sup> H, <sup>14</sup> C, Cl, CFCs, EJ)	If pre-industrial (>150 years), do not analyze for OM <sub>s</sub> ; if pre-tritium (>55 years), do not analyze for recently developed OM <sub>s</sub> like CFCs and recently developed pesticides and pharmaceuticals

EJ by expert judgment; OM<sub>s</sub> organic micro contaminants; AOX absorbable organically-bound halogens; VOX volatile organically-bound halogens; CFCs chlorofluorocarbons



purification methods and should even reduce their complexity in future. For this purpose and by order of the Ministry of Public Housing, Spatial Planning and the Environment (VROM), the Dutch National Institute of Public Health and Environment (RIVM) developed a protocol in order to compile all information relevant to water quality at the abstraction site in the so-called 'Dossiers for the area' (Wuijts et al. 2007). This information can be subsequently used to develop effective protection measures and will apparently be anchored in the National Drinking Water Act. The HCSA here presented could also be included in the 'Dossiers for the area', as a means to characterize PSWFs according to the groundwater origin and main hydrochemical facies, which indicates the processes affecting the quality of the water they deliver.

### Application for groundwater resources management

One of the major capabilities of the HCSA is the translation of complex hydrochemical patterns and processes into easily interpretable maps of groundwater bodies and hydrochemical facies, which can improve the communication between researchers, water resources managers and policy makers. The HCSA can be the key to solving complex groundwater resources management problems at different scales. In regards to a single well, it can be applied to quantify its vulnerability, by identifying pollution sources and hydrochemical processes responsible for its water-quality deterioration, and to optimize the monitoring program required to follow them up. On the scale of a PSWF, the HCSA reveals hydrochemical patterns within the well field that can be used to design a proper management strategy for the individual wells and optimize their pumping regime to guarantee the best quality of the raw water delivered by the PSWF. The results of the HCSA can also be used to decide the best

location and screening depth of a new well when more capacity is required, or to choose the wells to close in order to reduce capacity or improve the quality of the whole well field.

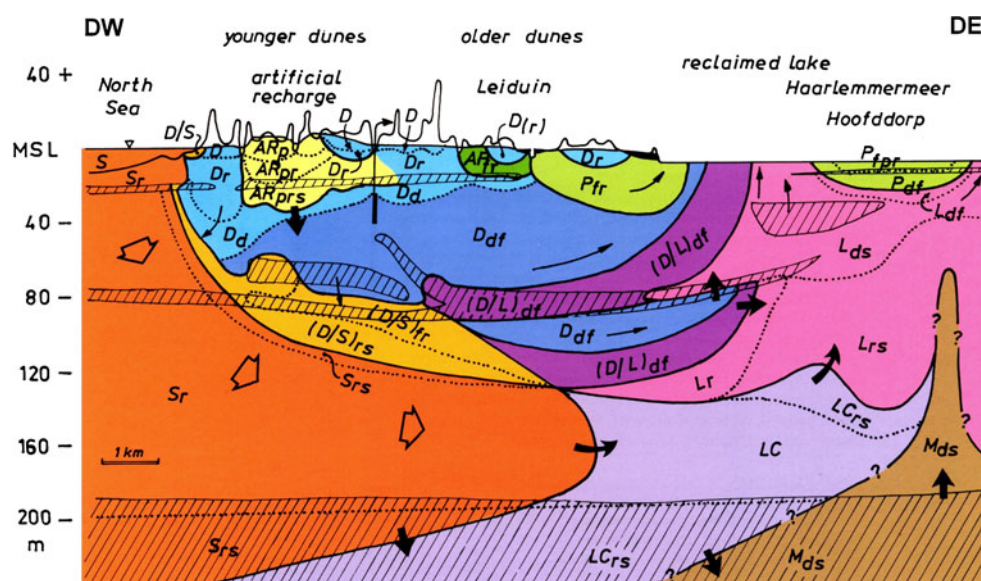
Figure 5 shows the results of the HCSA in its original form, for a cross section in the coastal dunes of Amsterdam, which have been artificially recharged with pretreated Rhine water since 1957. The HCSA has been applied in The Netherlands to create detailed maps of the whole coastal area (Stuyfzand 1993) and for AR and RBF systems in particular (Stuyfzand et al. 2006).

Figure 5 reveals the extent of five hydrosomes, in order of decreasing age: (M) connate, marine water, which was co-deposited with the Maassluis Formation at the beginning of the Pleistocene Epoch, about  $2 \times 10^6$  years ago; (L) relic, Holocene transgression waters, which were formed between 8,000 and 300 years ago during the various Holocene transgressions; (S) 'Actual' North Sea water, which infiltrated and still infiltrates through the actual sea floor, with a significant acceleration since the reclamation of lakes; (D) fresh, coastal dune water, which started to form about 5,000 years ago when the first beach barriers were left behind an advancing shore line; and (P) polder water, which mainly consists of Rhine River water (flushing and irrigating the polders) and local rainwater, less than 500 years old.

Within each hydrosome, various facies were discerned by a combination of: (1) the redox level, determined as indicated in Table 3; (2) the calcite saturation index (calcite being the dominant dissolving mineral); (3) the pollution index POLIN, which is based on six equally weighted quality aspects; and (4) the base exchange index, BEX, which indicates (ancient) salt or freshwater intrusion (for details see Stuyfzand 2008a).

Figure 5 is presented here as an example of application of the HCSA to conventional observation wells. Further detailed interpretation of the hydrochemical patterns

**Fig. 5** Cross section of the coastal dunes of Amsterdam, showing the areal distribution of hydrosomes with their hydrochemical facies as based on 200 well distributed samples (after Stuyfzand 1993). Line of section DW–DE shown in Fig. 1. Arrows indicate present groundwater flow. Codes are defined as follows: Hydrosomes: AP artificially recharged polder; AR River Rhine (artificially recharged); D dune; L relict Holocene transgression, marsh type; M connate Maassluis; P polder; S North Sea. Hydrochemical facies: a acid; d deep anoxic (methanogenic); f freshened; p polluted; r reduced and s salinized





obtained from the HCSA is beyond the scope of this contribution, but a detailed analysis is available in Stuyfzand (1993).

The HCSA can easily be further upscaled to develop strategic plans on the availability of groundwater resources and their protection, on a regional scale. A water-supply company can use it to optimize the management of its groundwater resources by regulating production rates of individual PSWFs according to their vulnerability or quality, and also to decide which PSWFs to expand or close down, in order to guarantee their demands at the lowest purification costs or with reduced complexity of purification technology, in compliance with the Water Framework Directive. Further upscaling to a national or European level is also feasible. A three-dimensional map of groundwater bodies and hydrochemical facies on a European scale could serve as a means to (1) summarize the quality status of European groundwater resources, (2) visualize the extent of GWBs, also in transboundary aquifers; and (3) follow up their growth and size reduction, which is more difficult to achieve with many single value maps of specific parameters.

## Conclusions

Public supply well fields (PSWFs) constitute an attractive (inter)national monitoring system for evaluating the chemical state of groundwater in order to safeguard drinking-water resources and monitor the environment. They are monitored on a regular basis as an integral part of the quality surveillance of national drinking-water supply and they have been so for a long time. They have also been extensively used in national groundwater surveys on various indicator parameters, but what was lacking, however, was a systematic approach to combine all relevant data into a clear typology of PSWFs. The hydrochemical system analysis (HCSA) here presented is such an approach, which combines all relevant data in order to better understand the individual state of and spatial patterns in groundwater quality delivered by PSWFs, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The origin is to be determined by environmental tracers, geomorphological and potentiometric maps, the facies by combining age, redox and alkalinity indices. The PSWF typology obtained provides a means to predict PSWF vulnerability, optimize groundwater-quality monitoring programs and better delineate groundwater bodies, by considering groundwater origin and flow. The latter also covers the need to delineate groundwaters bodies with artificial recharge and river-bank filtration, which are rapidly increasing in number and volume in many countries by the popularity of these methods for the production of clean safe drinking water and for storing surface water underground.

The HCSA translates complex hydrochemical patterns into easily interpretable maps by showing PSWFs,

groundwater bodies and hydrochemical facies. Such maps can become a key to solve complex groundwater resources management problems at different scales, ranging from a single well(field) or region to the national or European scale. They facilitate communication between researchers, water-resources managers and policy makers and show what is more difficult to achieve with single value maps of specific parameters.

The HCSA provides EU members with a means to redefine the boundaries of their GWBs as defined for the Water Framework Directive, in areas where the HCSA yields better results, with more homogeneous GWBs, more logically delimited for water-quality protection purposes and better extrapolated in depth following groundwater flow. A three-dimensional map of such groundwater bodies and hydrochemical facies on a European scale could serve as a means to summarize the quality status of European groundwater resources, to visualize the extent of GWBs and to follow up their dynamics (growth and shrinking), which is not possible with single value maps of specific parameters. The HCSA has the potential to become the basis for consistent rationalization of water management strategies and of compliance with the EU Directives.

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